



Catalytic performance of ionic liquid for dehydrochlorination reaction: Excellent activity and unparalleled stability



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ABSTRACT

Gas phase catalytic process with the advantages of simply product separation and maximized atom economy, which was a green path used in industrial production. At present, heterogeneous dehydrochlorination catalysts are facing challenge of rapid deactivation caused by released HCl and carbon deposit. In this paper, a series of supported ionic liquid catalysts (SILCs) was synthesized by wet impregnation method and applied to 1, 1, 2-trichloroethane (TCE) dehydrochlorination to produce 1, 1-dichloroethylene (VDC). Tetraarylphosphonium chloride was the active component with the unique acid resistance and the ability to dissolve coke, which determined the activity and stability of the catalyst. For 6%Tetraphenylphosphonium chloride (TPPC)/SiO₂(260 °C, WHSV = 0.19 h⁻¹), the conversion of 1, 1, 2-TCE was > 99.5%, selectivity of VDC was 86%, and the catalytic activity remained stable within 1100 h. Herein, highly activity for dehydrochlorination was attributed to the strong hydrogen-bond basicity of Cl-, which was decided largely by the interaction between anion and cation of ionic liquid. The reaction mechanism was investigated using FTIR, XPS, TGA-MS, XRF, DFT calculation and two step elimination model induced by alkaline active center is proposed. Such catalysts provide a viable industrial solution to gas dehydrochlorination reaction and design of heterogeneous basic catalysts.

1. Introduction

1, 1-Dichloroethylene(vinylidene chloride, VDC), one of the most important polymer monomers, which can be polymerized to produce polyvinylidene chloride (PVDC) in industry. PVDC is the sole material that has been approved by the FDA as one of first-class food and drug packaging materials [1], which is widely used in developed countries owing to its unique advantages, such as excellent sealing, safety and high temperature resistance [2–4]. 1, 1, 2-Trichloroethane (TCE) dehydrochlorination reaction is the main source of VDC, which can be carried out in both liquid and gas phase conditions. Homogeneous catalytic dehydrochlorination can be taken place under mild conditions and it is the main technology of industrial production. At present, 1, 1, 2-TCE liquid phase dehydrochlorination is commonly used in the industry by employing the NaOH and Ca(OH)₂ as catalyst, which exhibits high yield of VDC. However, hydrogen chloride (HCl) generated during the reaction would react with the alkali to form salts, and a large amount of salty wastewater is produced, which not only pollutes the environment, but also aggravates the HCl recycling. In contrast, HCl

can be removed and no wastewater will be produced in gas phase reaction, which is a green route.

However, there are some challenges in 1, 1, 2-TCE gas phase dehydrochlorination reaction. Firstly, the released HCl can be easily adsorbed on the basic active site, causing irreversible poisoning of the catalyst [5]. Secondly, due to the carbon deposition of VDC, the catalysts show much of the instability [5]. The catalyst reported in the literature was rapidly deactivated in 3–9 hours (pulse feed 2 μL/h of 1, 1, 2-TCE, maximum pulse times: 11 times) [6–12]. Thirdly, the catalytic performance of these catalysts was not ideal (low activity) [12]. In addition, the catalyst for the preparation of VDC from gas phase dehydrochlorination reaction has not yet been fully developed. Generally, 1, 1, 2-TCE dehydrochlorination catalysts should have these basic features: alkaline active sites, an appropriate interaction strength ought to be between Cl and basic site, the strong interaction will poisoning catalyst, and the weak interplay that is difficult to activate C–H bond of 1, 1, 2-TCE. Fortunately, ionic liquid (IL), a simple molten salt composed of anion and cation, which was liquid at room temperature [15,16] with the unique nature of acid resistance and the ability to

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dissolve synthetic polymers [13,14]. From the first synthesis of the IL by Waldn. P in 1914, ILs have been rapidly developed [17,18]. The special solubility of ILs and the adjustable of acidity and alkalinity have made them successful application in catalytic reactions [13,19–26], which inspires us to introduce them to dehydrochlorination reaction. High cost and difficulty in recycling are two major obstacles limiting IL's large-scale application, which can be solved by immobilizing IL on porous materials to synthesize supported ionic liquid catalyst (SILC) [27]. SILC was usually applied in heterogeneous catalytic reaction but homogeneous reaction occurred in the IL layer, which bridging heterogeneous and homogeneous catalysis reaction [28]. Such advantages make the topic of immobilized IL get great attention recently [29].

Herein, tetraalkylphosphonium chlorides with high melting point were used as the active species to synthesis the SILC, and applied it to prepare VDC via 1, 1, 2-TCE gas phase dehydrochlorination reaction. Moreover, a possible reaction mechanism was further proposed based on X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence (XRF) and density functional theory (DFT) calculation.

2. Experimental

2.1. Materials

Silica carrier (Specific surface area was $411.7 \text{ m}^2/\text{g}$, Pore volume was $0.9008 \text{ cm}^3/\text{g}$, the average pore size was 8.752 nm) was purchased from Qingdao Baisha Catalyst Factory (Qingdao, China). Methyltriphenylphosphonium chloride (MTPPC, 98%) was purchased from Energy Chemistry co. Ltd. (Shanghai, China) Ethyltriphenylphosphonium chloride (ETPPC, 98%) was purchased from Macklin Biochemical co. Ltd.(Shanghai, China). Butyltriphenylphosphonium chloride (BuTPPC, 98%) was purchased from Aladdin Industrial Corporation (Shanghai, China). Tetrabutylphosphonium chloride (TBuPC, > 99%) was purchased from Lanzhou Zhongke Kateke Industry & Trade Co. Ltd. (Lanzhou, China). Tetraphenylphosphonium chloride (TPPC, 98%) was purchased from Energy Chemistry Co.,Ltd.(Shanghai, China). Benzyltriphenylphosphonide chloride (BzTPPC, 99%) was purchased from Macklin Biochemical co. Ltd. (Shanghai, China). 4-Fluorobenzyltriphenylphosphonium chloride (FBzTPPC, > 98%) was purchased from Adamas Reagent, Ltd. (Shanghai, China). Methanol (> 99.5%) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). Absolute ethanol (99.7%) was purchased from Anhui Ante Food Co. Ltd. (Soochow, China). 1, 1, 2-Trichloroethane (1, 1, 2-TCE 99%) was purchased from Aladdin Industrial Corporation (Shanghai, China).

2.2. SiO_2 pretreatment

A certain amount of SiO_2 was immersed in nitric acid (1.0 mol/L) for three hours with assisted by a stirrer. The soaked SiO_2 was washed with deionized water until the pH of the washings became neutral, then placed it in a blast oven, dried at 100°C for 12 h, then which was placed in a muffle furnace roasting at 800°C for 6 h. After the completion of the treatment, the SiO_2 was stored in a sealed bag filled with nitrogen.

2.3. Catalyst preparation

The catalyst was prepared by impregnation method. The pure IL (Supplementary Table 1) was dissolve in 20 mL of absolute ethanol, and an amount of pretreated SiO_2 was added to IL-ethanol solution, then the mixture was put into an ultrasonic cleaner for 1 h and let stand for 12 h at 25°C . The impregnated catalyst was placed in a blast drying oven and dried at 100°C for 12 h. The dried catalyst was stored in a sealed bag filled with nitrogen.

2.4. Catalytic performance tests

A quantity of catalyst was filled to the fixed bed reactor and the reactor was heated with heating belt. 1, 1, 2-TCE was fed into the reactor by bubbling method. Nitrogen was used as the carrier gas, and the reaction product was absorbed by methanol, which was detected using Agilent gas chromatography 7890A (analysis conditions was in Supplementary Information). A circulating cryogenic was employed to control the temperature of the bubbling feeder and the absorption bottle bath. Details see Fig. 1 in Supplementary Information for the reaction device.

2.5. Catalyst characterizations

The Thermogravimetric analysis (TGA) of the catalyst was taken on a NETZSCH STA 449 C with QMS 403C (Mass spectrometry), used air atmosphere (99.99%) 30 mL per minute and Argon (99.999%) 30 mL per minute, heating rate: 10°C per minute. Fourier transform infrared spectroscopy (FT-IR) was taken on a Nicolet 6700 Fourier transform infrared spectrometer, Nicolet Continuum infrared microscopy system. Brunner-Emmet-Teller (BET) measurements was taken on the micromeritics ASAP2020 automatic surface area meter. Nuclear magnetic resonance (NMR) was taken on a Bruker AVANCE III 500 MHz, dissolved 0.03 g IL into CDCl_3 solution. X-ray Fluorescence (XRF) analysis was taken on an American ThermoFisher company ARL ADVANT'X IntelliPowerTM 4200 at vacuum environment. Scanning electron microscope - Energy dispersive spectroscopy (SEM-EDS) was taken on a FEI Nano nova 450 field emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) was taken on an ESCALAB 250Xi with an Al $\text{K}\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$) and binding energies referenced to C1s (284.8 eV).

3. Results and discussion

3.1. Activity of catalysts

1,1,2-TCE gas phase catalytic dehydrochlorination reaction was carried out at a temperature in the range of 200 – 300°C [5], since the temperature is one of the main limitation for ILs. The ILs used here are quaternary phosphonium chloride salts with a high decomposition temperature [30], and chloride ion (anion) itself is resistant to hydrogen chloride, which is a decisive factor in our choice of those ILs. Several SILCs with a fixed loading of 6% (Wt. %) were fabricated and their catalytic activity was evaluated in a fixed bed reactor (Supplementary Fig. 1). The results are shown in Fig. 1a,b.

As shown in Fig. 1a, b, except for FBzTPPC and BzTPPC, other catalysts have no deactivation behavior, and SiO_2 has no activity (selectivity of VDC was 0%). TPPC shows the best catalytic performance, followed by MTPPC, ETPPC and BuTPPC. The 1, 1, 2-TCE conversion of TPPC was 100%, and the VDC selectivity was 85%; while, the 1, 1, 2-TCE conversion of MTPPC, ETPPC and BuTPPC was 95% and the VDC selectivity was 87%. The catalytic activity of TBuPC was relatively lower than that of MTPPC and TPPC, with a conversion of 1, 1, 2-TCE was 87% and a selectivity of VDC was 89%. The activity of BzTPPC and FBzTPPC decreased significantly during the reaction, which may be due to the volatilization or decomposition of these ILs. Overall, the SILCs show significantly different conversions of 1, 1, 2-TCE, with the less difference in selectivity of VDC. The order of catalytic activity is TPPC > BuTPPC > ETPPC > MTPPC > TBuPC > BzTPPC > FBzTPPC. The difference in activity may attribute to the divergence in the proton accepting ability of the IL's anion (Cl^-). The reason for the difference in the ability of Cl^- to accept protons is the interaction between anions and cations. That is, the stronger the interaction between the anions and cations of IL, the weaker alkalinity of anions [31,32]. With increasing length of the alkyl side chain, the interaction between Cl^- and P_{666X}^{+} (P_{4444}^{+}) increases, and the Proton Accepting Ability

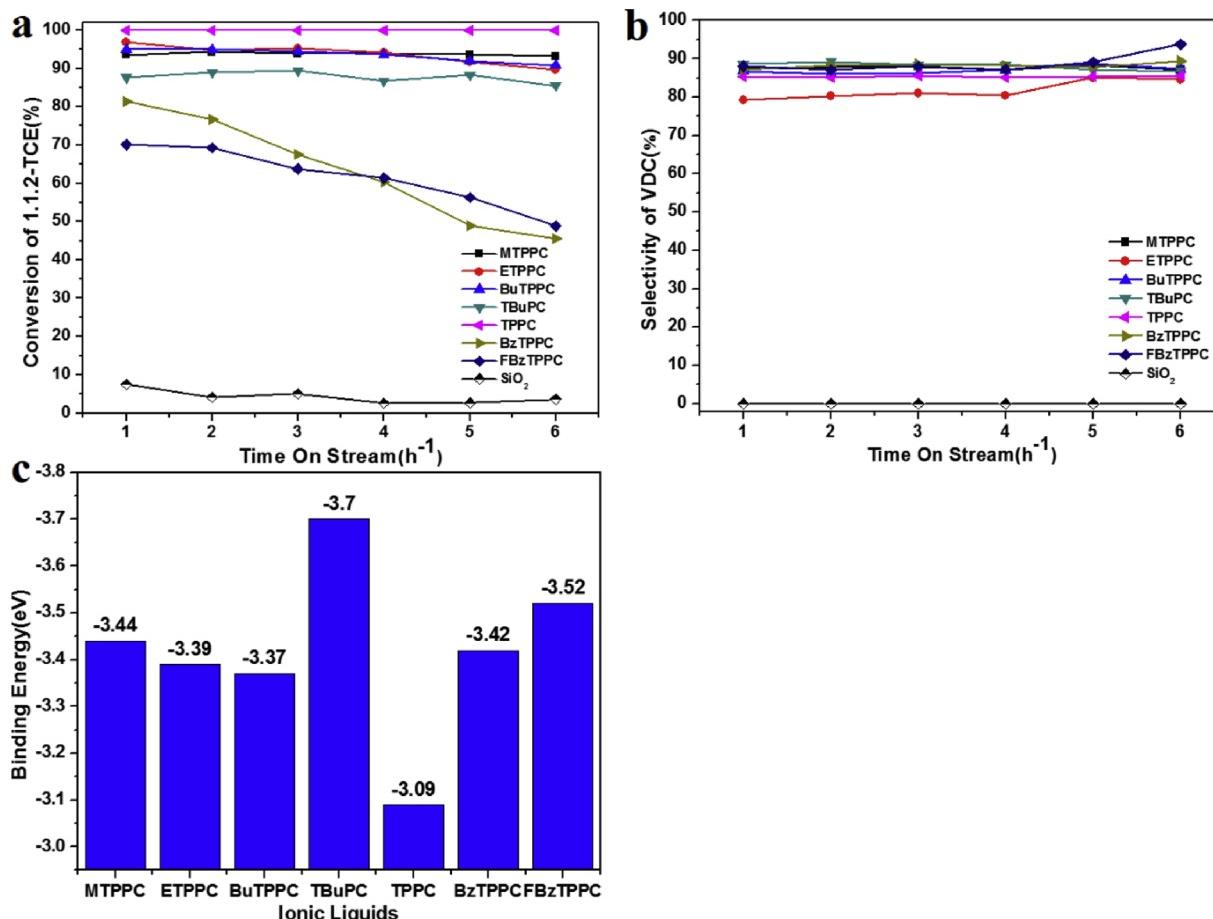


Fig. 1. Catalytic activity of SILC and result of DFT calculate, (a) Conversion of 1,1,2-TCE; (b) Selectivity of VDC; (c) Binding energy of cation-anion of IL by DFT calculation. Reaction conditions were as follows: temperature: 260 °C, catalyst usage: 3 g, 1,1,2-TCE feed amount: 0.025 g/h, nitrogen flow rate: 10 mL/min, the temperature of the bubbling feeder and the absorption bottle was 0 °C.

(hydrogen bond basicity) of Cl⁻ increases accordingly. The enhancement of the basicity of the catalyst was beneficial to the reaction of 1, 1, 2-TCE dehydrochlorination to generate VDC [5]. For supporting the hypothesis, DFT calculation was carried out to calculate the interaction between the anions and cations of the ILs [33,34]. All structural optimizations and frequency calculations were performed at the level of B3LPY/6-31+G (d, g) [35] using Gaussian 09 package [36]. The binding energy between the cation and anion of IL was calculated using Equation (1)

$$E_b = -[E_{C-A} - (E_C + E_A)] \quad (1)$$

Where E_b is binding energy, E_{C-A} is binding energy of cation and anion, E_C is energy of cation and E_A is energy of anion. The calculation results are shown in Fig. 1c and the result of structural optimizations is shown in Supplementary Fig. 2. It is clear that the binding energy between the anion and cation of IL decreases with the growth of alkyl side chain length. The binding energy of different IL followed the order TBuPC > FBzTPPC > MTPPC > BzTPPC > ETPPC > BuTPPC > TPPC. The binding energy between the cation of TPPC and Cl⁻ was the smallest, which may be attributed to the symmetric cation. When the length of side chain increased from methyl group to butyl group, the change of interaction energy was small, which was consistent with the negligible difference in catalytic activity of the three ILs (MTPPC, ETPPC and BuTPPC). The binding energy between anion and cation of TBuPC was greatly higher than that of TPPC, and its activity was significantly reduced. The interaction between BzTPPC cation and Cl⁻ increase may be due to the larger benzyl group. This effect is stronger than the decrease in binding energy caused by the increase in the

distance between anions and cations. The activity of BzTPPC and FBzTPPC was also significantly lower than that of TPPC because of the high binding energy. The ability of IL used here to catalyze dehydrochlorination of 1, 1, 2-TCE was ascribe to the weaker interaction between anion and cation, which is far less than dissociation energy of NaCl (4.23 eV) [37]. The advantage of IL catalyzing the gas phase dehydrochlorination is that the interaction between the cation and the anion (Cl⁻) so weak as to endow the strong hydrogen-bond accepting ability of anion, which catalyzed dehydrogenation reaction. The interaction between anion and cation of TPPC(3.09 eV) is the smallest and the activity was highest, which confirmed the weaker interaction of anion and cation in favor of catalyzing dehydrochlorination reaction.

3.2. Exploration of reaction conditions

Due to its excellent performances, this work will main focus on TPPC/SiO₂. The important factors such as the reaction temperature and loading of the IL concerned with catalyst was investigated. Fig. 2 presents the effect of temperature in dehydrochlorination reaction. It is noted when the temperature raised from 200 °C to 260 °C, the conversion of 1,1,2-TCE and selectivity of VDC were increased rapidly, and the conversion of 1,1,2-TCE reached 100% at 260 °C and 280 °C. The results were corresponded with that gas dehydrochlorination was an endothermic reaction. Since TPPC has a melting point of 265–267 °C [38], the IL layer in the molten state may facilitate the reaction. However, higher temperatures are not conducive to the stability of the IL. Thus, 260 °C is chosen as the target reaction temperature.

Even though many studies were concentrated on the distribution of

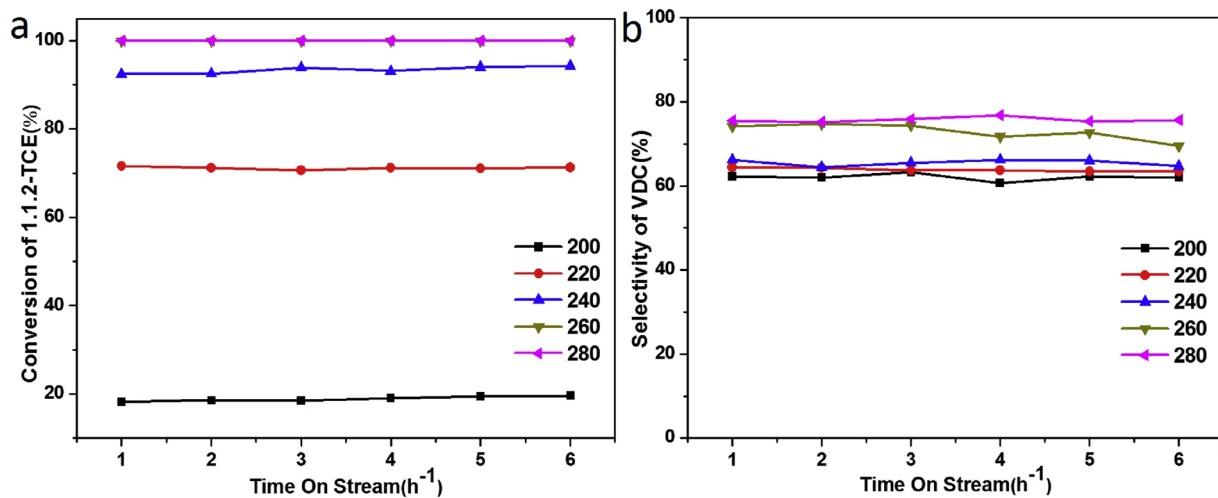


Fig. 2. Catalytic activity of 15%TPPC/SiO₂ at different temperature. (a) Conversion of 1, 1, 2-TCE; (b) Selectivity of VDC. Reaction conditions were as follows: temperature: 200 °C, 220 °C, 240 °C, 260 °C, 280 °C, 15% TPPC/SiO₂ usage 1.2 g, The 1, 1, 2-TCE feed amount was 0.025 g/h, N₂ = 10 mL/min, the temperature of bubbling bottle and absorption bottle was 0 °C.

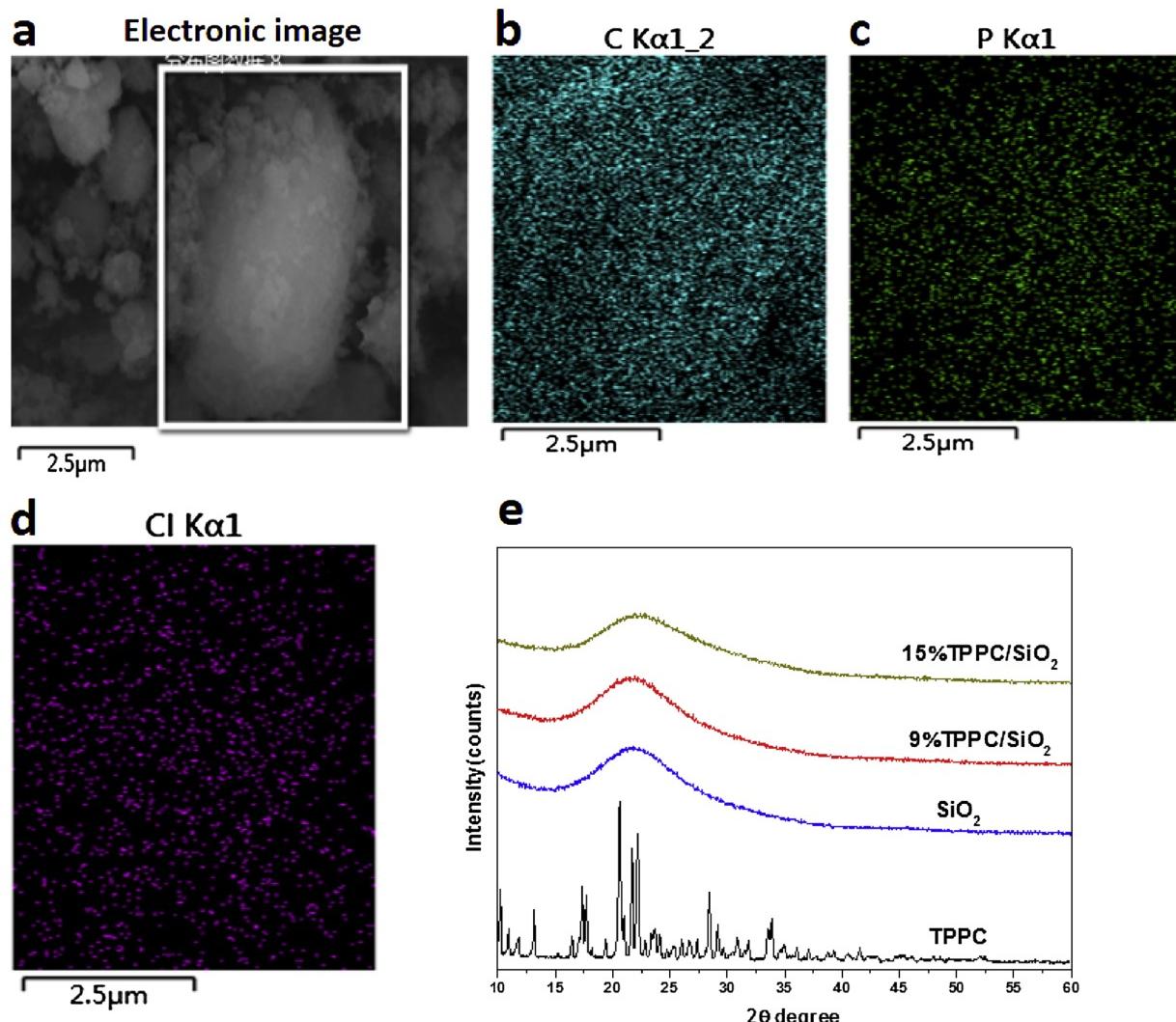


Fig. 3. (a-d) Scanning Electron Microscope and Energy Dispersive Spectroscopy (SEM-EDS) of 6%TPPC/SiO₂; (e) X-ray Diffraction (XRD) patterns of TPPC, SiO₂, 9%TPPC/SiO₂ and 15%TPPC/SiO₂.

Table 1
Result of EDS element analysis.

Element	Apparent concentration	Wt%	Atom%
C	5.4	28.98	34.37
P	0.52	0.97	0.46
Cl	0.02	0.07	0.03

ILs on the different materials surface have been reported [39–43], the study about the distribution of TPPC on the silica surface is still lacking. In order to study the condition of TPPC supported on silica surface, X-ray diffraction (XRD) was performed to analyze the pure IL and SILCs. Through Fig. 3e, we found that a strong diffraction peak appears in the XRD pattern of TPPC, which confirmed that the pure TPPC is crystalline. Interestingly, the diffraction peak of TPPC disappeared after immobilizing TPPC onto the silica surface. It is believed that the TPPC did not form crystals, but coated on the surface of silica. Quantitative analysis of the EDS spectrum (Fig. 3 a–d) shows the atomic distribution of P, Cl and C of 6% TPPC [44,45]. It suggests that C, P and Cl element distributed evenly without agglomeration or island distribution, and the anion and cation regular covered on the horizontal surface of silica. Table 1 and Supplementary Fig. 7 presents the elemental analysis of the silica surface. The density of C atoms is more than 24 times higher than that of P atoms, and the density of P atoms is 15 times higher than that of Cl atoms, resulting from the various distribution of IL's cations and anions on the vertical direction interface between silica and IL. The distribution condition is that the phenyl group approaches the gas phase, and the Cl^- is towards the silica surface. Further, we used the materials studio software to simulate the distribution of TPPC on the silica surface. All structural optimizations and calculations were carried out at the level of GGA/PW91/DN by DFT methods in Material Studio 6.1 package [58]. The model was shown in Supplementary Fig. 5 that Cl^- of TPPC located closed to Si atom of silicon and cation lay up to Cl^- , which is in accord with the EDS analysis.

The thickness of the IL layer on the silica surface varies with the different loadings of the IL, which may affect the activity of the catalyst. For understanding this factor, TPPC/SiO₂ with different loading was prepared and their activity was evaluated. It is clear in Fig. 4a, b that with the decrease of the loading, both the conversion rate of 1,1,2-TCE and the selectivity of VDC showed an upward trend. The conversion of 1, 1, 2-TCE of 3% TPPC/SiO₂ and 6% TPPC/SiO₂ reached 100%, and the selectivity of VDC was 82% roughly. It is likely benefit from the increased amount of carrier and the thinner IL layer, the area of 1,1,2-

TCE contacting with the IL as well as the conversion rate increases with IL loading decreases. Further, it can be concluded from Supplementary Fig. 4 that as the increasing loading, the IL is coated on the silica surface and blocked part of the microporous channels, resulting in a decrease in pore volume and specific surface area, and an increase in the average pore diameter. From the pore size distribution (Supplementary Fig. 2), it is evident that the number of micropores was significantly reduced in 15%TPPC/SiO₂ compared with silica, and the distribution of mesopores shifted drastically. Concurrently, the selectivity of VDC increased with the IL loading decreasing, which may be due to that the dehydrochlorination reaction prefers to occur in thinner IL layer. To explore this factor, XPS characterization of the catalysts with different loadings was performed. It is shown in Fig. 5 a, b.

It is clear in Fig. 5a, b that XPS spectra of P2p and Cl2p of pure TPPC are consistent with previous report [46]. The binding energy of P shifts to a high position from 132.6 eV (15%TPPC/SiO₂) to 133.2 eV (6%TPPC/SiO₂) with the decreasing loading, indicating an electron offset between the IL and the silica surface [47,48]. When the loading was less than 12%, the peak positions of the Cl2p and P2p unchanged, indicating that the IL was a monolayer on the surface of silica [47,48]. Also, the steric effect has a large influence on the surface distribution of the IL in the pores of the carrier [49], which may affect the chemical environment of cations or anions. The chemical environment of Cl with a binding energy of 197.2 eV is similar to that of Cl in $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{C}_{60}]\text{Cl}$ [50], which may occur in double IL layer as shown in Fig. 5c. The binding energy of 200.5 eV is a covalent state of Cl [50], indicating that the IL layer tends to be monolayer to generate a strong interaction with silica surface. The change in binding energy of Cl2p is due to the different dispersion of IL from the bulk to the covering on the silica surface. To understand the single layer of TPPC on silica surface, we simulated the distribution of TPPC on the silica surface (Supplementary Fig. 6) using Material Studio software and found that Cl ion was close to Si atom of silica. The distance between Cl^- and Si atom was 2.215 Å, indicating a strong hydrogen bonding between Cl- and Si atom [51]. Futuremore, when the loading decreased, the Cl2p peak (197.2 eV) intensity of the two-layer IL gradually reduced, and the peak (200.5 eV) strength of the single-layer IL increased, suggesting that the IL is finally dispersed in single layer. Form the model shown in Fig. 5c, it is believed that TPPC follows two dimensional (2D) expansion when the loading is low, and then three dimensional (3D) growth as loading increasing. Hence, when the IL layer is thinned, the number of phenyl group around Cl- reduced, which is more easily for H atoms of 1, 1, 2-TCE to contact with the Cl- of the IL and catalyze the dehydrochlorination reaction. It is clear that Cl- plays a key role in the catalytic

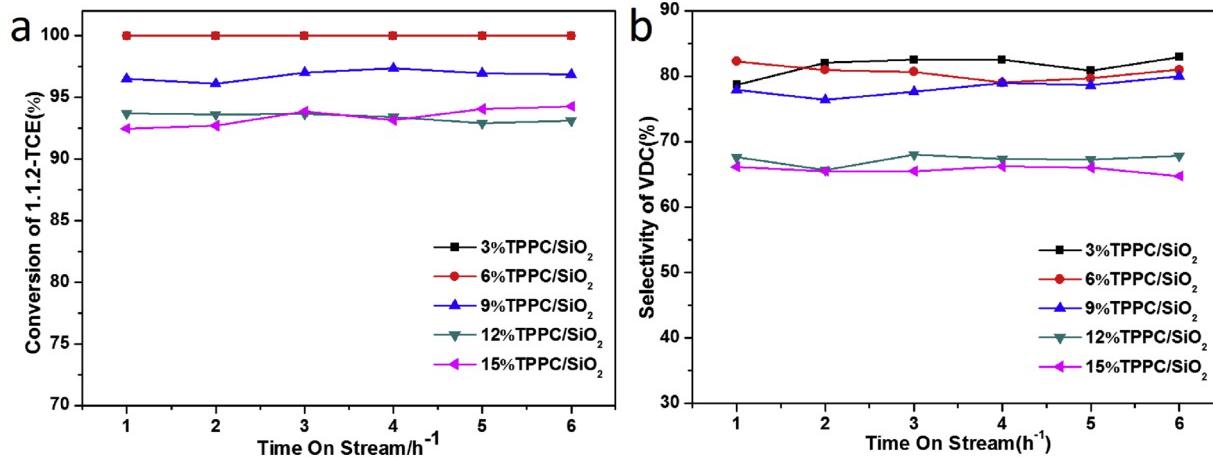


Fig. 4. Catalytic activity of catalysts with different TPPC loadings. (a) Conversion of 1, 1, 2-TCE; (b) Selectivity of VDC. Reaction conditions were as follows: temperature: 260 °C, the amount of TPPC used in the reaction remained the same: 0.156 g, the amount of catalysts used were 15% TPPC/SiO₂: 1.2 g, 12% TPPC/SiO₂: 1.5 g, 9%TPPC/SiO₂: 2 g, 6% TPPC/SiO₂: 3 g, 3% TPPC/SiO₂: 6 g, 1,1,2-TCE feed amount was 0.025 g/h, N₂ = 10 mL/min, and the temperature of the bubbling bottle and the absorption bottle was 0 °C.

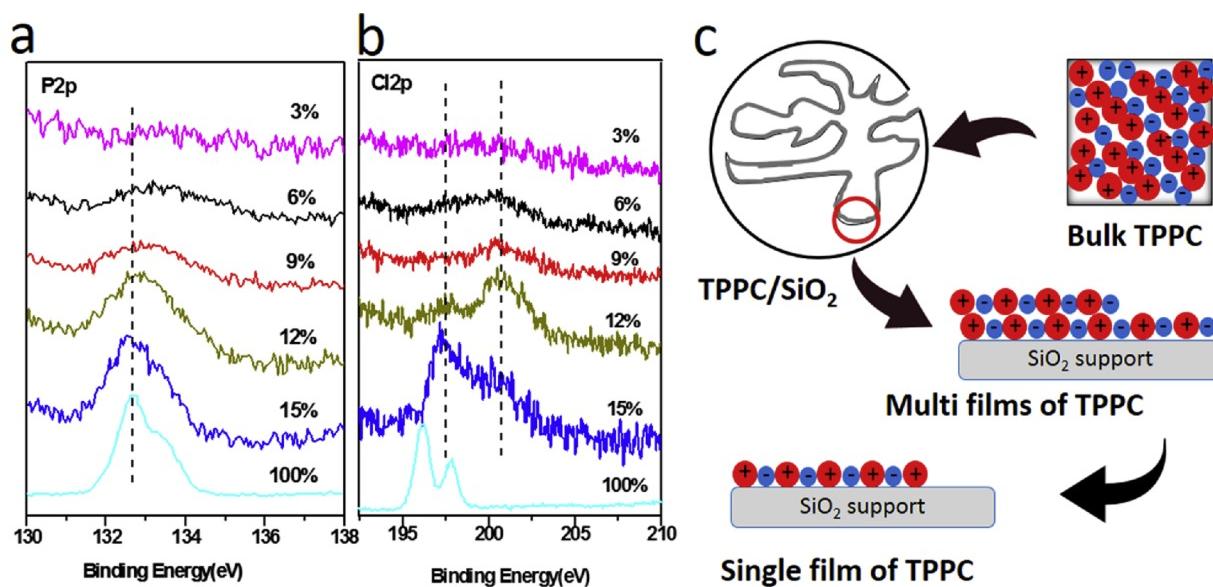


Fig. 5. (a) P 2p & (b) Cl 2p X-ray Photoelectron Spectroscopy (XPS) of the TPPC/SiO₂; (c) IL distribution model from bulk to single film.

dehydrochlorination process, and the thickness of the IL layer is a major effect on the activity of the SILCs through steric hindrance.

3.3. Stability and life of TPPC/SiO₂

To demonstrate the stability of our catalysts, 6% TPPC/SiO₂ was prepared and the activity evaluated by increasing feed rate of 1, 1, 2-TCE during 50 h as shown in Fig. 6a. 1, 1, 2-TCE feed rate increased from 0.0250 g/h to 0.0484 g/h and 0.0827 g/h making the conversion decreased from 100% to 76% and 74%, and selectivity of VDC reduced from 82% to 65% and 62%. It is noted that the activity of the catalyst is slightly decreased with the increasing mass space velocity but changed little during 50 h, which indicates the excellent stability of 6% TPPC/SiO₂. To investigate whether carbon deposits had occurred in TPPC/SiO₂, TGA-MS was performed in air atmosphere with a heating rate of 10 °C per minute on the used catalyst (1,1,2-TCE feed rate 0.0484 g/h, reaction was carried out at 260 °C for 50 h). TGA-MS analysis (Fig. 6b) showed two weight loss peaks of the used catalyst in the differential thermogravimetric (DTG) curve (black), which were 382 °C and 620 °C respectively. The differential scanning calorimetry (DSC) curve (blue) showed that the weight loss at 382 °C was endothermic, and the weight

loss at 620 °C was exothermic. Furthermore, there was a weaker exothermic peak at 412 °C. Combined with mass spectrometry data, it was found that HCl was released below 412 °C, followed by CO and CO₂ as the temperature rises. The exothermic peak at 412 °C was attributed to the decomposition of PVDC [52], and the weight loss peak at 630 °C to the oxidative decomposition of triphenylphosphine oxide, because no signal peak of HCl appeared at this temperature. Therefore, there was a trace amount of carbon deposit produced during the reaction, which may be located on the silica surface, not on the IL layer surface. Nevertheless, it should be noted that carbon deposition did not affect the activity of the catalyst, because IL used here has the ability to dissolve synthetic polymers [13,14], and polymerization reaction cannot occur in IL layer. From the perspective of economy and industrial application, the catalyst lifetime is an important feature for heterogeneous catalysis, therefore the durability testing of 6%TPPC/SiO₂ was carried out under the WHSV = 0.19 h⁻¹ of 1, 1, 2-TCE at 260 °C, and the result is shown in Fig. 7. It is noted that the unprecedented stability of 6%TPPC/SiO₂, which is much longer than that reported in the literature [5–12]. Within 1100 h of the reaction, the conversion of 1, 1, 2-TCE was > 99.5%, the selectivity of VDC was about 86% and with no decrease during the period.

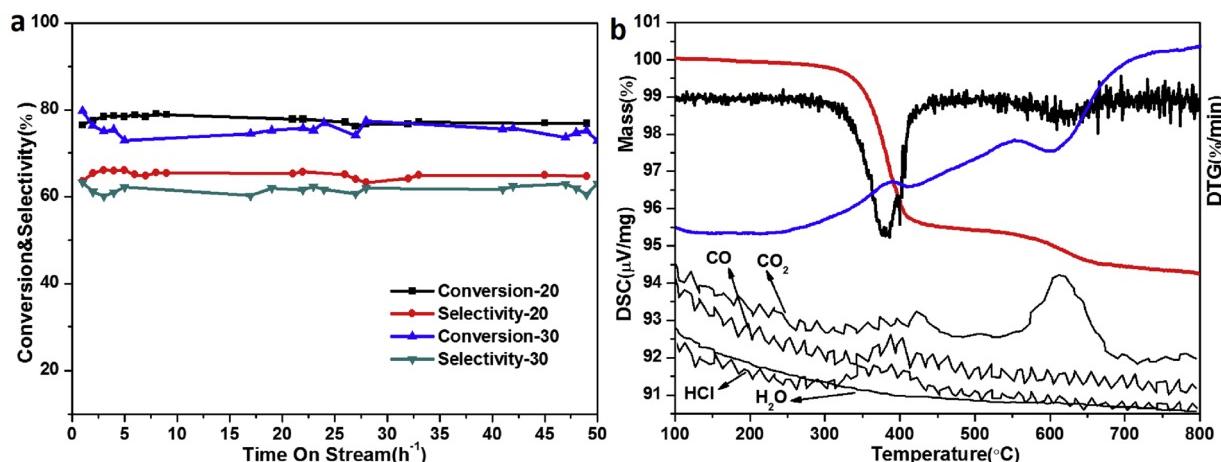


Fig. 6. (a) Catalytic stability test of 6% TPPC/SiO₂ via increasing feed rate of 1,1,2-TCE; (b) Thermogravimetric analysis-Mass spectrometry(TGA-MS) curves of the fresh and used 6%TPPC/SiO₂. Reaction conditions: temperature: 260 °C, feeding bottle temperature: 20 °C, 30 °C, N₂ = 10 mL/min, absorption bottle temperature: 0 °C, The feeding rate of the feeding bottle at 20 °C was 0.0484 g 1, 1, 2-TCE per hour, and at 30 °C was 0.0827 g 1, 1, 2-TCE per hour. Catalyst usage: 3 g.

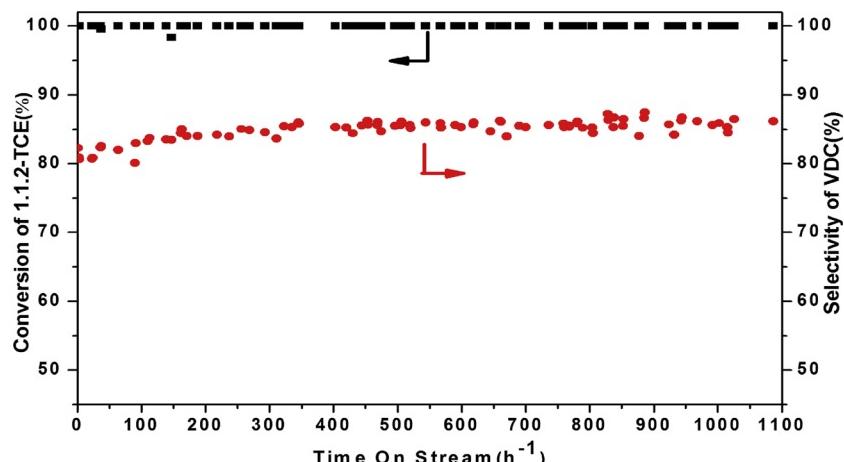


Fig. 7. Catalytic life of 6%TPPC/SiO₂. Reaction conditions were as follows: temperature: 260 °C, 1, 1, 2-TCE feed amount: 0.025 g per hour, feeding bottle and absorption bottle temperature: 0 °C, N₂ = 10 mL per minute, and catalyst usage: 3 g.

3.4. Reaction mechanism

TPPC/SiO₂ gas phase catalyst for synthesizing VDC exhibits high activity, excellent stability and unprecedented lifetime. The long-term stability is based on two main reasons: firstly, HCl removed from 1, 1, 2-TCE is not toxic to TPPC because the Cl exists as anion of TPPC. The interaction between the cations and anions of the IL is weaker than the traditional metal chloride, which reduces the possibility of poisoning IL [25]. Also, the IL we used has good physical and chemical stability, and the decomposition temperature of TPPC is high (above 300 °C) [30]. Secondly, IL could dissolve synthetic polymers that solves the challenge of coke. By testing the specific surface area and pore size distribution of the prepared catalyst (Supplementary Fig. 3,4), it was indicated that TPPC was successfully loaded onto the silica surface. To detect the functional group of the carrier's surface, FT-IR of SiO₂, TPPC and 15% TPPC/SiO₂ was carried out. Fig. 8a presents the infrared spectrum of TPPC, which was consistent with that reported in the literature [53]. According to the previous study [54], 2850–2960 cm⁻¹ was the C–H vibration peak, 1440 cm⁻¹ was the skeleton vibration peak of the benzene ring, and 724 cm⁻¹ and 690 cm⁻¹ were the in-plane bending vibration peaks (monosubstituted) of the C–H of the benzene ring. There was no absorption peak of the chemical bond between Cl and Si in the FT-IR spectrum, indicating that TPPC is successfully loaded onto the surface of silica, and the interaction between TPPC and the carrier is the physical adsorption [55].

In order to investigate the stability of chemical structure of ILs during the reaction, we tested the ¹³C-NMR and ³¹P-NMR spectra of TPPC before and after the reaction, which is shown in Supplementary Fig. 5. It is found that there was no difference between the NMR spectra of fresh TPPC and that after the reaction, and the peak positions of the TPPC were consistent with those reported in the literature [56], which indicated that the chemical structure of TPPC remained stable during the reaction, proving that TPPC played a role as catalyst in the reaction process rather than reactant. It has also been reported that 1, 1, 2-TCE dehydrochlorination reaction was acid-base synergistic-catalyzed E2 elimination or E1cb elimination mechanism induced by basic center, or E1 elimination mechanism catalyzed by acid sites [5]. The selectivity of VDC improved as the strength of the basic active center increase [5]. The anion of the IL used in this work has the ability to accept H⁺, which act as a Lewis base in the reaction. While, the basic strength of the anion is related to the interaction between the anion and the cation [25,31,32]. When the carrier was used as a catalyst, only by-products were detected as shown in Fig. 1a, b, because the silica has silanol groups on the surface, which can only catalyze side reactions. TPPC/SiO₂ catalyzes the 1,1,2-TCE gas phase dehydrochlorination with a VDC

selectivity of 85%, and the selectivity of cis-1,2-dichloroethylene and trans-1,2-dichloroethylene are 7% and 8%, respectively. This product distribution is in line with the results that 1, 1, 2-TCE dehydrochlorination induced by basic center [5], which suggests the mechanism of this reaction might be E1cb. To further study the reaction mechanism, a series of 15% TPPB/SiO₂ was prepared. One (1.2 g) set at 260 °C for 24 h with 0.025 g / h of 1, 1, 2-TCE; and the other one introduced 1 mL/min of HCl under the same reaction conditions for 6 h. We conducted X-ray Fluorescence Spectroscopy (XRF) to analyze the element content of fresh TPPB and TPPB treated by 1, 1, 2-TCE and HCl. It is clear in Fig. 8b that after the introduction of 1, 1, 2-TCE, the Br element in TPPB disappeared, and the content of Cl increased greatly with no change in P content, indicating that the substitution between Cl and Br occurred during the reaction. After the introduction of HCl, the Cl element replaced the Br element, and the content of Cl increased slightly than that after the introduction of 1, 1, 2-TCE, which may attribute to the partial dissolution of HCl gas in the IL. TPPB has the ability to activate HCl [57], when HCl was adsorbed on the surface of TPPB, the bond between hydrogen and chloride was split, followed by the formation of HBr. Cl⁻ then interacts with tetraphenyl cation, and replaces the position of Br⁻, which is in agreement with the previous result.

The interaction between anions and cations of TPPC and TPPB was calculated using the DFT calculation method, and the bond energy of C–Cl after removal of H⁺ from 1, 1, 2-TCE is shown in Fig. 8c. It suggests that the binding energy between anions and cations was TPPB (-3.42 eV) > TPPC (-3.09 eV), which indicates that the reaction mechanism of TPPC is the removal of H⁺ and then combination with the Cl⁻ of TPPC to synthesis hydrogen chloride. The C–Cl bond energy of another side C atom can be greatly reduced and easy to be broken. The removed Cl⁻ supplements the lost anion of the TPPC, ensuring the charge balance and structural stability of the TPPC and formation of a catalytic cycle.

Fig. 9 presents the possible reaction mechanism in TPPC/SiO₂ catalyzing 1, 1, 2-TCE gas phase dehydrochlorination to prepare VDC. Firstly, 1, 1, 2-TCE diffuses to the surface of the catalyst and then adsorbs on the surface of the TPPC. The chloride ion of TPPC interacts with the α-hydrogen atom (more acidic than other hydrogen atoms) of 1, 1, 2-TCE, and then induces C–H bond cleavage. H⁺ is bonded with Cl⁻ of the TPPC to form hydrogen chloride. The tetraphenylphosphine cation (P₆₆₆₆⁺) interacts with the chlorine atom on β-C atom of Cl₂C⁻–CH₂Cl to break the C–Cl bond to form VDC. The eluted Cl⁻ replaces the lost anion in the TPPC at the second step, maintaining the electrical neutrality and integrity of the TPPC. VDC desorbs from the surface of the TPPC and diffuses to the gas phase. Under the synergistic

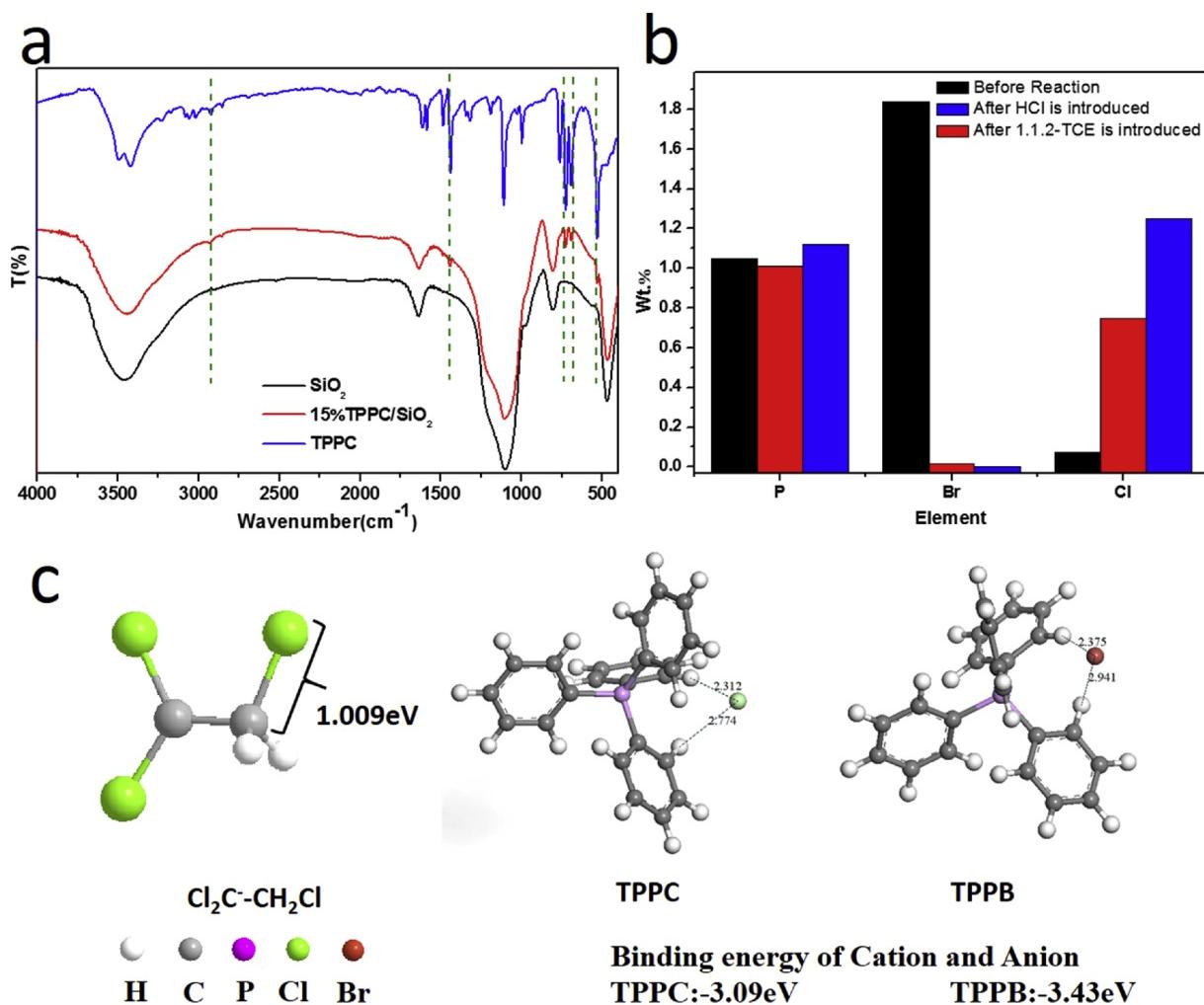


Fig. 8. (a) Fourier transform infrared spectrum (FT-IR) of SiO_2 , TPPC and 15% TPPC/ SiO_2 , the absorption peaks marked by dotted line were 2926 cm^{-1} , 1441 cm^{-1} , 724 cm^{-1} , 690 cm^{-1} , and 528 cm^{-1} , respectively; (b) X-ray Fluorescence Spectroscopy(XRF) of 15% TPPB/ SiO_2 before and after the reaction; (c) Bond energy of C-Cl and binding energy of cation and anion calculated by DFT theory.

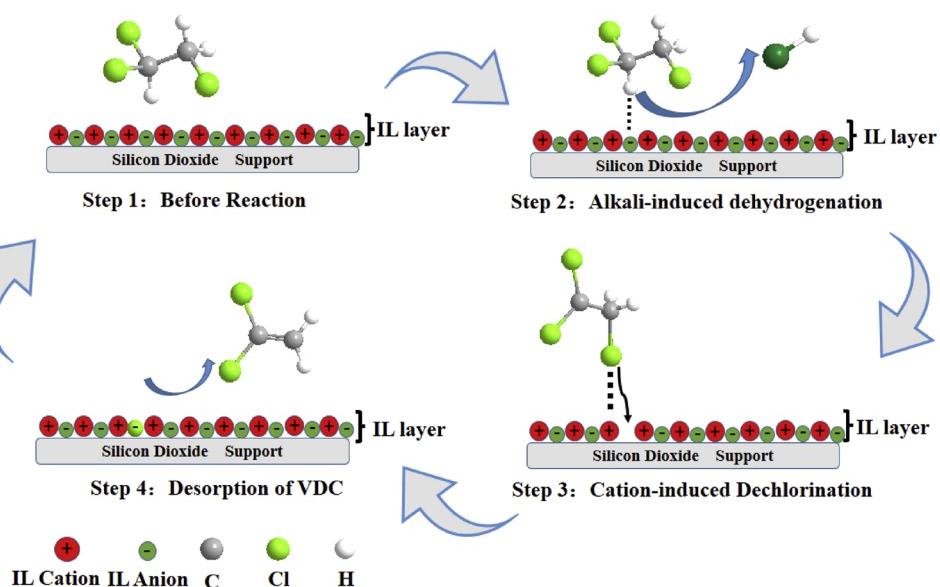


Fig. 9. Possible reaction mechanism in TPPC/ SiO_2 catalytic 1, 1, 2-TCE gas dehydrochlorination.

catalysis of the TPPC anion and cation, 1, 1, 2-TCE successively undergoes dehydrogenation and dechlorination to form HCl and VDC, which is a typical E1cb elimination reaction. On the surface of SiO₂ uncovered by IL, 1, 1, 2-TCE dehydrochlorinates under the catalysis of silanols to form trans-1, 2-dichloroethylene and cis-1, 2-dichloroethylene.

4. Conclusions

A series of SILCs was prepared successfully and was applied to the gas phase dehydrochlorination reaction of 1, 1, 2-TCE. TPPC/SiO₂ exhibited excellent activity and unprecedented stability as well as an extremely long lifetime by solving the challenges of acidosis and carbon deposit at one time. The 1, 1, 2-TCE conversion was > 99.5%, the VDC selectivity was 86%, and no deactivation occurred during the 1100 h evaluation period. Weak interaction of anion and cation made IL an excellent catalyst in dehydrochlorination reaction. It was found that single layer IL was beneficial to the reaction because fewer benzene rings around the Cl⁻ environment of the single-layer IL than bulk IL. Furthermore, the reduction of the steric effect of benzene group made the hydrogen atom of 1, 1, 2-TCE more easily interact with Cl⁻. A variety of evidences demonstrate that the gas phase dehydrochlorination reaction of 1, 1, 2-TCE in TPPC/SiO₂ was basic center-induced two step reaction model. Herein, we are firstly apply the SILC to the 1, 1, 2-TCE gas phase dehydrochlorination reaction, which increased the likelihood of industrialization of 1, 1, 2-TCE gas phase dehydrochlorination. This paper provides a reference for the design and preparation of heterogeneous non-metallic alkaline catalyst and expands the application range of the SILCs, which enriches the IL catalysis theory for the catalytic mechanism and the SILC.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.117757>.

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